Reinforcement of Natural Rubber/Ethylene-Propylene-Diene Monomer (NR/EPDM) by Silane Functionalized Halloysite Nanotubes

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Abstract

We describe a nanocomposite made of halloysite nanotubes (HNTs, a naturally occurring tube-like nanoparticle), natural rubber (NR), ethylene-propylene-diene monomer (EPDM), and ethylene-propylene-diene monomer grafted with maleic anhydride (EPDM-g-MA). Diethoxydimethyl silane (DMS), a silane coupling agent, was used to modify highly hydrophilic HNT nanotubes to ensure proper dispersion of these nanoparticles in the hydrophobic NR/EPDM rubber matrix. After the silane modification, the functional groups on the surface of the HNTs were characterised and the degree of modification was determined using field emission scanning electron microscopy (FESEM). The maximal tensile strength, stress at 100% elongation (M100), and elongation at break are reached at 8 phr after the addition of DMS modified HNTs to NR/EPDM. Any additional growth causes the tensile strength, M100, and elongation at break to gradually decline.

1. Introduction

Numerous studies have discussed how different types of rubber blends are prepared and characterised [1–4]. By utilising the desirable qualities of the blend's constituent materials and avoiding the financial and technical risks involved in the synthesis of new polymeric materials, rubber blending creates new materials with a wide range of uses [5–7]. In addition, the wide range of appealing rubber blend systems that have been extensively studied, including SBR/NBR [2], NBR/EVA [3], NBR/HNBR [4], NR/SBR [8], NR/BR/EPDM [9], NR/SBR/BR [10], NBR/EPDM [11–12], NR/BR [13], have amply shown the overwhelming need to find adaptable blends capable of meeting particular performance requirements for particular technological applications. Due to their excellent performances in tyres and other demanding applications, the vulcanised NR/EPDM systems have received the most attention of these [6, 14–22]. Researchers have been drawn to further investigate and improve the formulation of NR/EPDM compounds as a result of the NR/EPDM blends' notable increases in heat and ozone resistance [17]. A tiny amount of a nonconjugated diene is used to polymerize ethylene and propylene to create EPDM, a saturated carbon-hydrogen polyolefinic rubber [5, 12, 16]. The addition of this rubber phase to elastomer or thermoplastic elastomeric blends (TPE) imparts good ageing characteristics, including weathering and oxidation, as well as thermal and chemical resistances [16, 22]. EPDM is frequently employed as an impact modifier [23]. However, due to the nonpolar and unsaturated properties of this synthetic rubber phase, the inclusion of EPDM in the formulation of rubber blends causes significant incompatibility and immiscibility issues [24].

NR is significantly more unsaturated than EPDM and chemically reactive [19]. NR is particularly prone to degradation even though it has outstanding elasticity, fatigue resistance, high resilience, and exceptional strength properties, as well as a low level of strain sensitivity and strong processing characteristics [5, 25]. Additionally, due to the reactivity of the double bonds in the main chain, NR is susceptible to environmental variables such ozone, light, moisture, humidity, radiation, and heat [5, 14, 26, 27]. Because of this, many high-performance industrial applications are no longer viable for using NR [28]. Therefore, the limits of NR can be overcome by combining it with a low unsaturated rubber phase, such as EPDM (highly saturated and non-reactive) [14]. The selective diffusion of curatives towards the NR phase in any of their corresponding blends, on the other hand, has been brought on by a higher cross-linking rate of NR [16]. The propensity for the production of crosslinks in the EPDM phase may be further decreased by the lower solubility of many curatives in the EPDM phase [20]. This situation adds to the blend's uneven cure distribution and the phases' poor interfacial adhesion, which cause significant incompatibility and immiscibility issues between NR and EPDM [16, 20], which stimulate the degradation of the blend's attributes and subpar performance [17]. As a result, it is very desirable to be able to create almost any two or more polymers to interact chemically with each other [21] when creating a variety of stable rubber mixes.
Some of the research works that have been engaged to enhance the rubber compatibility of the EPDM-based blends are slight procuring of EPDM before blending, modification of EPDM rubber matrix with reactive materials like maleic anhydride (MA) [6], employment of different compatibilizers and accelerators that have superior solubility with EPDM rubber phase [19, 21], radiation technique [22], EPDM functionalization using carboxylated and halogenated compound [25], addition of a third rubber such as epoxidized natural rubber (ENR) to performance as a compatibilizer [28], mercapto-modified copolymer [29], rubber compounding technique, and addition of inorganic nanoparticles as a stabilization and an absorption agent at the interface of the rubber blends [14, 17]. A successful strategy for creating modified rubber blends with enhanced qualities has been the grafting of rubber phase with various functional monomers [20, 30]. A common example of a chemical with two distinct functions used to compatibilize rubber mixes via reactive blending techniques is MA or citric acid (or its hydrate) [31]. The maleated polymer and filler have an affinity for each other due to the anhydride's polar nature, which can act as a compatibilizer and enhance interactions between the matrix and filler [30, 32]. Additionally, the grafting of EPDM with MA results in an elastomer with local polarity and chemical reactivity [9]. In addition, after reviewing related studies conducted by earlier researchers on EPDM grafted with MA [23, 24, 33, 34], we discovered that the mechanical properties of the vulcanised blends of the functionalized EPDM with NR significantly improved [9] if the EPDM molecules were functionalized by MA or maleic acid. This is due to the MA group, which gives the EPDM additional polarity and connects to a highly polar double bond of the NR diene rubber phase [9]. The EPDM phase's cross-link density is similarly increased by MA modification, probably because more polarity promotes the dispersion of curatives favourably [35]. In addition, Tavakoli et al researcher's [36] showed that EPDM-g-MA is a more effective compatibilizer than the frequently used ENR50 in NR filled nanoclay nanocomposites. This observation led to the selection of EPDM-g-MA as a reactive compatibilizer agent to enhance the interaction between NR and EPDM, as the compatibility of the two rubbers is the primary determinant of the blends' attributes.

Over the past few decades, polymer research has largely focused on the development of polymer composites including different nanoparticles, which has captured the attention and curiosity of experts all over the world [37–42]. Due to their significantly improved mechanical [43–44] and thermal properties [45] compared to conventional composites, especially at low clay loadings, clay-based polymer nanocomposites have recently garnered a lot of attention. Because nanoparticles have a propensity to aggregate, homogeneous dispersion of nanoparticles is a challenge for polymer nanocomposites. Lamellar clays, particularly laponite [46–47], smectite [48], kaolinite [49–50], and montmorillonite [51–52], make up the majority of the clay minerals under investigation. This study looked into the organosilane functionalization of [53–54] halloysite (Al₂(OH)₄Si₂O₅·2H₂O), a naturally occurring tubular clay material. This is a naturally occurring aluminosilicate nanotube, and very little is known about how it might be used in rubber composites. Halloysite nanotubes (HNTs) are a two-layered aluminosilicate that resemble kaolin chemically and have a predominantly hollow tubular structure in the submicron range. According to Bates et al. [55], the wall curves into a cylindrical shape due to an imbalance in the two-layered alignment of the tetrahedral sheet of silica that is linked to the octahedral or gibbsite sheet of alumina. The spiral wall's repeated two-layered sheets may include intercalated water, which is often irrevocably removed upon drying. The resulting deposit can be exploited for the economically feasible substance halloysite as a raw mineral. According to the deposits, the size of halloysite particles vary between 1 and 15 µm in length and 10 to 100 nm in inner diameter. In comparison to other nanofillers, it provides a higher amount of filler-polymer interactions because to its high aspect ratio (L/D). HNTs are a new type of filler that has recently been employed to improve the mechanical and thermal properties of composites made of polymers including epoxy, polypropylene, and polyvinyl alcohol [56–59].
Due to its interaction with the hydroxyl groups and the layered architecture of the substance, HNT is a hydrophilic mineral that holds a large amount of water molecules. Additionally, it has hydroxyl groups at the margins of the tubes and the outside surface of the inner lumen [60]. It is preferable to alter these minerals using a silane coupling agent in order to use this nano-sized filler in a hydrophobic rubber matrix. 3-Aminopropyl triethoxysilane (APTES, H\(_2\)N(CH\(_2\))\(_3\)Si(OC\(_2\)H\(_5\))\(_3\)) was used to modify HNT, and Yuan et al. examined the surface properties of HNT [61]. In order to enhance the thermomechanical performance of the composites, HNT has also recently been investigated as a novel type of filler for incorporation into plastics including epoxy, poly(vinyl alcohol), and polypropylene [62–64]. Recent studies on nanocomposites based on HNT that contain NR, EPDM, and carboxylated styrene butadiene rubber have demonstrated excellent mechanical qualities in terms of tensile strength, elongation at break, and thermal properties [65–67]. Finding new fillers that are appropriate for rubber matrix and can provide even greater mechanical qualities is a significant task.

HNTs resemble multi-walled carbon nanotubes (MWCNTs) in appearance, but they differ from MWCNTs in terms of their low density of hydroxyl functional groups, unique crystal structure, and tubular shape, which makes them easier to disperse in polymer matrices [68–72]. To investigate the potential of modified HNTs nanofillers in NR/EPDM/EPDM-g-MA composites is the goal of this article. This work reports the impact of modified HNTs content on the morphology, swelling and abrasion resistance, tensile properties, and curing parameters of NR/EPDM/EPDM-g-MA nanocomposites.

2. Experimental

2.1 Materials

NR: Grade - Ribbed Smoked Sheets (RSS)-1, density – 0.9125 g/cm\(^3\), ash content – 0.58%, ML\(_{(1 + 4)}\) 100°C – 57 M, and nitrogen content – 0.63% were procured by Asian Rubber Pvt. Ltd., Ambattur, Chennai, India.

EPDM: Grade - KEP-270, density – 0.86 g/cm\(^3\), ethylene content – 68 wt.%, termonomer content (ethylidene norbornene) – 4.5%, ML\(_{(1 + 4)}\) 125°C – 60 M, and volatile content – 0.4% were supplied by Supple Rubber Chemicals Pvt. Ltd., New Delhi, India.

Halloysite nanotubes (family: kaolin clay), diameter x length: 30–70 nm x 1–3 µm, linear chemical formula: Al\(_2\)Si\(_2\)O\(_5\)(OH)\(_4\)·2 H\(_2\)O, and molecular weight: 294.19 g/mol, and silane coupling agents, diethoxydimethyl silane (DMS, (CH\(_3\))\(_2\)Si(OC\(_2\)H\(_5\))\(_2\)) were obtained from Sigma-Aldrich, Puducherry.

Activator (stearic acid and ZnO), Zinc diethyldithiocarbamate (ZDC), accelerators (mercaptobenzothiazyl disulphide – MBTS, and tetramethylthiuram disulphide - TMTD), and 2-mercaptobenzothiazole – MBT) and vulcanizing agent (sulphur) were contributed by Vignesh Chemicals Pvt. Ltd., Ambattur, Chennai, India.

Ethylene-propylene-diene rubber grafted with maleic anhydride (EPDM-g-MA), with the trademark Bondyram® 7001, was purchased from Songhan Plastic Technology Co. Ltd., Shanghai City, China with melt flow rate (MFR) of 7 g/10 min (ASTM D D1238), mass density of 0.87 g/cm\(^3\) (ASTM D792) and MA content of 0.7%.

Benzene, mesitylene, toluene, xylene, n-pentane, n-heptane, n-hexane, n-octane, chloroform, dichloromethane, and carbon tetrachloride were all supplied by Sigma-Aldrich, Puducherry. Everything that was received was utilised.

2.2 Preparation of DMS-HNT
As a result of their hygroscopic nature, HNT nanotubes were dried at 105°C for 1 hour before usage. In order to modify the HNT in bulk, 60 grammes of the substance were used. 300 ml of dry toluene was added to the dried HNT in a flask with a circular bottom. The mixture was then mixed with 4ml of DMS, and the flask was immediately sealed. Following a 30-minute at-room-temperature ultrasonication of the mixture, the contents of the flask were refluxed for 72 hours at 70°C. Using guard tubes filled with calcium chloride and Teflon tapes, a dry environment was maintained during this operation. The system was cooled to room temperature after the reaction period in less than an hour. To eliminate the unreacted DMS, the DMS-modified HNT (hence referred to as DMS-HNT) was filtered through a sintered funnel and washed three times with toluene. With the aid of a mortar and pestle, the DMS-HNT was ground to a powder after drying at 50°C for two hours. Finally, desiccators were used to hold the DMS-HNT in order to create a dry atmosphere [73].

2.3 Characterization of the modified HNTs Fillers

Through an immersion test, changes in surface polarity were investigated. A little amount of filler was added to the surface of a solvent, in this case water, to conduct the test. Due to their hydrophilic surfaces, the original HNTs sink right away, whereas the modified fillers should float for a longer period of time. A water penetration test produced more precise data. This test involved filling a glass column with 0.02 g of filler and covering the opening with two layers of a hydrophobic filter with a pore size of 0.2 m. The column was submerged in water, and the weight shift brought on by water absorption was tracked over time.

2.4 Preparation of NR/EPDM/modified HNTs nanocomposites

Table 1 provides the nanocomposites’ formulations. Blends of NR/EPDM (75:25 phr) were created using traditional mixing techniques in an open-mill mixer. First stage (80°C): The NR rubber was first ground in the mill for about 5 minutes, and then EPDM-g-MA was added and mixed with the EPDM rubber for about 3 minutes. Then, the following vulcanization materials were added in that order: modified HNTs, ZnO, stearic acid, MBTS, TMTD, ZDC, and MBT. Second stage [74–75]: Using the same mill at 70°C for 3 min, fully Vulcanised compounds were made by adding sulphur. Depending on the filler loading, the compounding time for each nanocomposite was maintained for 20 to 30 minutes.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Compounds (phr)</th>
<th>NR</th>
<th>EPDM</th>
<th>EPDM-g-MA</th>
<th>Modified HNTs</th>
<th>Zinc oxide</th>
<th>Stearic acid</th>
<th>MBTS</th>
<th>TMTD</th>
<th>ZDC</th>
<th>MBT</th>
<th>Sulphur</th>
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</thead>
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<tr>
<td>mH₀</td>
<td></td>
<td>75</td>
<td>25</td>
<td>5</td>
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<td>4</td>
<td>1.5</td>
<td>1.2</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>2.5</td>
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<td>5</td>
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<td>4</td>
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<td>1</td>
<td>1</td>
<td>1</td>
<td>2.5</td>
</tr>
</tbody>
</table>
The Zwick 4308 rheometer was used to analyse the characteristics of the unvulcanized rubber samples at 160°C in accordance with ASTM D2084 standard. At the aforementioned temperature and equipment, the vulcanization behaviour of composites, including the optimum cure time \( t_{90} \), the time for the completion of cure, the scorch time \( t_{S2} \), the time for the onset of cure \([76]\), the maximum torque \( M_h \), the minimum torque \( M_l \), the delta torque \( M \), and the cure rate index (CRI), a parameter proportional to the average slope of the cure curve \((100/(t_{90} - t_{S2}))\) in the curing.

For curing, a typical vulcanization procedure was employed. According to each composite's individual \( t_{90} \) as established by a Zwick 4308 rheometer instrument, compression moulding of all composites was performed utilising a hydraulic hot press at 160°C and a force of 30 MPa.

### 2.5 Characterization

By using an ODR rheometer at 160°C in accordance with ASTM D-2084, the curing properties of nanocomposites were assessed. According to ASTM D-412, tensile characteristics were assessed using C-type Dumbbell specimens on a Universal Testing Machine (UTM) (series: 7200, make: Dak System Inc., model: T-72102). Using a Wallace die cutter, the specimens with dumbbell-shaped dimensions of 2 mm in thickness, 25 mm in breadth, 115 mm in overall length, and 33 mm in gauge length were cut into standard test pieces. A 500 mm/min crosshead speed was chosen. Each composite underwent testing on at least five samples. Then, for each case, the average value of the data surrounding the average value were computed and reported.

The resistance of a material to tear forces is gauged by its tear strength. By dividing the highest force by the specimen's thickness, the tear strength of a notched specimen is determined. Using unnicked 90° test pieces with dimensions of 102 mm overall length, 19 mm wide, and 12.7 mm in cutting edge length, the tear strength was evaluated in a UTM in accordance with ASTM D-624 (Die C). At 500 mm/min, the tear characteristics were evaluated. Each composite underwent testing on at least five samples. Then, for each case, the average value of the data surrounding the average value were calculated and reported.

Using a Zwick abrasion tester and the following conditions: emery paper grade 60, constant force of 10 N, and constant speed of 0.32 m/s, an abrasion test was conducted in accordance with ASTM D-5963. The results were expressed as abrasion loss, which is the volume in mm3 abraded from a test piece per 40 m. To guarantee uniformity in the findings, the average of five tests for each sample was run.

Using a durometer hardness tester device with a hardness range of 0 to 99 Shore A, the samples' hardness was measured in accordance with ASTM D2240. A vertical rebound resilience instrument in accordance with ASTM D2632 was used to study resilience.

By using the Flory-Rehner equation and quick solvent-swelling measurements (toluene uptake for 72 h at 23 ± 2°C), the crosslink density of the specimens was calculated:

\[
M_c \left( \frac{g}{mol} \right) = \frac{-\rho_p V_s V_r^{1/3}}{\ln (1 - V_r) + V_r + \chi V_r^2}
\]

\[
V_r = \frac{1}{1 + Q_m}
\]
where, $M_c$ – molecular weight, $\rho_p$ – density of the NR/EPDM rubber matrix, $V_s$ - molar volume of the solvent (106.3 ml/mol for toluene solvent), $V_r$ – volume fraction of the swollen rubber, $\chi$ - interaction coefficient between the rubber network and solvent (0.44), $Q_m$ - weight swell of the NR/EPDM nanocomposites in toluene.

Equation (3) yields the crosslink density ($v$) degree:

$$v \left( \frac{mol}{cm^3} \right) = \frac{1}{2M_c}$$

3

These nanocomposites' solvent absorption was calculated using published research [79]. For these tests, cured test samples with dimensions of 25 x 25 x 2 mm were weighed precisely (w0), then placed in airtight test bottles and submerged in toluene. The test samples were taken out of the solvent at regular intervals and dried between filter sheets to get rid of the extra solvent on their surface. They were then immediately weighed and submerged once more in the solvent to allow the kinetic sorption to continue until saturation in surplus liquid was achieved.

A compression device was used to measure the permanent compression set over a 24-hour period at 23°C, 70°C, and 100°C with a 25% form variation. The sample was then removed and left to sit at room temperature for 30 minutes. Then, it was measured for thickness. The following was the permanent compression set calculating method: Percentage of compression set, $C\% = \frac{T_0 - T_1}{T_0 - T_S} \times 100 \ (4)$

where $T_0$ - initial thickness, $T_1$ - final thickness, and $T_S$ – slip gauge distance.

Using a field emission-scanning electron microscope (FE-SEM) model Hitachi S-3400 working at a voltage of 30 kV, the tensile fracture surface was examined. The goal was to get a general understanding of the fracture mode. To prevent electrical charge during examination, the fracture ends of the tensile specimens were mounted on stubs and sputter coated with a thin layer of gold.

3. Results and discussions

3.1. Filler Characterization

The water immersion test was done to determine whether the hydrophobicity has changed: As anticipated, the untreated HNT powder instantly sank in water; but, following treatment, some of the substance floated on the water for a while. This demonstrates the decrease in polarity of the HNTs following DMS modification, but it also shows an uneven coating, which may be brought on by the inclusion of filler aggregates in the DMS modification process. Figure 1 displays the results of the water absorption. Both unmodified and DMS-modified HNTs gradually absorbed water, and after a while, an equilibrium level was reached. However, pure HNTs absorbed more water than DMS-modified HNTs, suggesting that DMS-modified HNTs are more hydrophobic. This exploratory study showed that DMS modified HNTs are less polar and more hydrophobic than the unmodified filler, suggesting that they might work better with a non-polar rubber matrix.

3.2. Cure properties
Table 2 displays various curing characteristics of rubber (NR/EPDM) matrix-modified HNT nanocomposites. When compared to modified HNT (DMS-HNT or mHNT) loaded NR/EPDM compounds, the gum NR/EPDM molecule exhibits a longer scorch time \( t_2 \). This demonstrates that the inclusion of HNT shortens the time required for rubber compound to scorch. This might be explained by the fact that HNT is alkaline, which encourages the vulcanization reaction. Modified HNT is incorporated to gradually reduce the composite's optimum cure time. The optimum cure time for compounds containing 10 phr modified HNT, however, is shorter than for compounds including gum. As a result, the modified HNTs function effectively as both a reinforcing agent and an accelerator or co-curing agent for the vulcanization process of the NR/EPDM matrix. Therefore, adding a tiny amount of mHNTs to NR/EPDM elastomer blends, which are often used in the automotive industry, would shorten the time needed for the vulcanization process. Cure rate index can be used to express how changing HNT affects the kinetics of NR/EPDM matrix cure (CRI). The average slope of the cure curve \( 100/t_{90}-t_{52} \) in the curing step region is a parameter that relates to CRI. The faster the curing process, the higher the CRI rating. With increasing mHNT loading, the CRI of modified HNT loaded NR/EPDM compounds rises. Thus, it can be concluded that the changed HNT has a direct impact on how quickly the NR/EPDM compounds cure. Therefore, the vulcanization process in NR/EPDM is improved by the presence of modified HNT in rubber compounds at larger proportions.

The volume percentage of modified HNT in the NR/EPDM matrix causes an increase in the minimum torque \( M_l \) and maximum torque \( M_h \). The 10 phr modified HNT filled NR/EPDM composites showed a greater torque. Thus, a greater degree of torque increase is due to the silanization reaction's and strong contact between the hydroxyl groups of the modified HNT and NR/EPDM matrix. The cure values shown in Table 2 demonstrate that, as anticipated, the torque difference \( M = M_h - M_l \) increases with the modified HNTs loading. It is thought that the bonding strength will increase with the reduction of the hydroxyl groups. This would result in stronger interactions between the rubber and the filler, adding more flow resistance and restricting the motion of the macromolecules more severely, raising the torque value. On the other hand, compounds containing mHNT particles will have greater torque values as a result of their higher crosslink density [80]. \( \Delta M \) is actually a measurement of the shear dynamic modulus, which has a tangential relationship to the crosslink density of nanocomposites [81]. Table 2 shows that torque values climb as the amount of nanotubes increases. Even though this would increase the amount of energy needed for the compounding process, it would be overlooked given the little amounts of mHNTs added to the blends and the benefits this approach offers.
Table 2  
Cure properties of the NR/EPDM-mHNT compounds

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Min. torque (dN m)</th>
<th>Max. torque (dN m)</th>
<th>Torque difference (dN m)</th>
<th>Scorch time (min.)</th>
<th>Optimum cure time (min.)</th>
<th>Cure rate index (min⁻¹)</th>
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</table>

3.3 Mechanical properties

HNTs are ideally suited for reinforcing in polymer nanocomposites due to their natural tubular morphology, nanoscale diameter, high aspect ratio, and contrasting chemistry on external and internal surfaces [82]. The enhanced mechanical capabilities are always explained by the effective transfer of external load from the polymer matrix to the HNTs. The majority of the research that has been published has been on the improved mechanical characteristics of polymers brought on by HNTs. The loading, dispersion, and interfacial interactions of the nanotubes in the systems were connected to the strength and modulus of HNTs-polymers. As is widely known, the material used for automotive parts’ abrasion resistance, tensile strength, and swelling resistance plays a crucial role in the final product’s quality. The main characteristics of the pure NR/EPDM/EPDM-g-MA compounds, which are frequently utilised in the automotive industry, could also be enhanced by nanotubes.

In addition to dispersion, a problem arises from the interaction of rather hydrophobic fillers and hydrophilic polymers. It is possible to increase compatibility by altering the polarity of the fillers. The surface properties of the fillers are often altered using various coupling agents, such as silanes. Usually, the coupling agents are included into the mixture while mixing. The silanization reaction between the coupling agent and the filler needs to be completed at a specific temperature and for a specific amount of time.

Pretreating the filler with DMS prior to use is an alternative. Since HNTs’ surface chemistry is similar to that of silica, it is anticipated that DMS treatment will be able to alter their surface. The following outcomes are possible by selecting the right monomer: (1) It is possible to decrease the polarity of the HNT surface, (2) shield the functional groups on the surface, particularly the hydroxyl groups, (3) switch the surface’s chemical make-up to hydrocarbons, and (4) introduce new functional groups into the surface.

Interpenetrating networks may be produced as a result of the formation of functional groups that can react with the polymer during curing: During vulcanization, a robust covalent filler-polymer network can also form in addition to the polymer-polymer network. In addition, the polymers’ sulphur, activators, and accelerators can influence the crosslinking reaction. The final material’s qualities will be affected by this.
There was a notable improvement in the mechanical properties of the NR/EPDM-mHNTs nanocomposites (tensile strength, stress at 100% elongation (M100), elongation at break, tear strength, and hardness), which are reviewed in depth and depicted in Figs. 2–6. Up to 8 phr HNTs, the tensile strength, M100, and elongation at break increased. Due to the production of tubular agglomerates, NR/EPDM composites filled with 10 phr modified HNTs showed a modest reduction in their characteristics. The tensile strength, M100, and elongation at break values of NR/EPDM composites with modified HNT, however, were higher than those of rubber matrix. The NR/EPDM nanocomposites' highest increases in tensile strength, elastic modulus, and elongation at break were 100%, 45%, and 53%, respectively, after the introduction of 8 phr modified HNTs. The chemical with the highest elongation at break value was also that one. The mHNTs’ surface-mounted sulphur moieties, which allow them to applying this technique with the polymer and create interpenetrating networks, have an effect on this. According to Fig. 9, the improvement in cross-linking density was what caused the tensile strength and M100 of the compatibleized NR/EPDM-modified HNTs composites to increase.

The nanotubes' greater interaction with the elastomer chains is created by their equal distribution. Elastomer chain mobility was constrained by its entanglement with the filler and the potent interfacial interactions between HNTs and rubber. A more efficient transfer of applied stress to nanotubes is also made possible by the wider contact. These factors help HNTs reinforced NR/EPDM composites have improved reinforcing and mechanical qualities. In the NR/EPDM nanocomposites, well-distributed modified HNTs minimise inter-particle distance, causing overlap of immobile elastomer chains at the interface regions. The production of HNTs aggregates was the cause of the loss in mechanical characteristics of the 10 phr mHNTs filler filled NR/EPDM with EPDM-g-MA, as indicated by the FE-SEM in Fig. 10. Agglomerates of HNTs tubes result in a non-uniform distribution of fillers and a decrease in the interactions between modified HNTs and rubber.

Additionally, the nanotube aggregates reduce the efficiency of load transfer from matrix to filler by increasing stress concentration at the filler-rubber interfaces. Better van der Waals forces, chemical bonds between the rubber matrix, the surface of modified HNTs and other physico-chemical interactions are also indirectly measured by the improved static mechanical behaviour of rubber nanocomposites reinforced with nanotubes. The mechanical behaviour of the nanocomposites may also be improved by the physical crosslinks that the HNTs nanotubes create. Accordingly, at HNT contents more than 8 phr, the mechanical property increase rate begins to slow down.

Hardness and tear strength of the NR/EPDM/EPDM-g-MA nanocomposite samples are plotted in Figs. 4 and 5, respectively. The interactions between the matrix and HNTs, the circumstances of compounding, the microstructure, and the HNT quantity all affect the mechanical strength of the nanocomposites. Brown et al. [83] claim that hardness is just a measurement of modulus. Similar phenomenon, i.e., a significant rise in the value of harness when the filler content is raised, can be seen in modulus measurements. As anticipated, increasing the HNTs content in comparison to the basal elastomer blend enhanced tear strength and overall hardness. The interaction between the rubber matrix and the nanofiller in the nanocomposite as well as the confinement of polymer chains in the presence of HNTs within the matrix have both been credited as causes for this improvement.

Ganeche and coworkers [84] speculate that the decrease in abrasion loss and rebound resilience shown in Fig. 6 may be caused by an increase in crosslink density in the presence of HNT. The probability of energy loss/dissipation increases with filler and plasticizer concentration. The energy loss at the filler-matrix interface, friction between the chains, or filler structural collapse can all cause energy dissipation. Lower resilience values will be the result of this. Although the rate of loss is lower at greater mHNT loading, the abrasion loss is still minimal. In actuality, the mHNT/matrix adhesion improves with increased aspect ratio HNTs. This increase may be explained
by the fact that some of the applied stress was supplied by the nanotubes, which decreased penetration into the polymer surface and allowed only microploughing and/or microcutting phenomena to be produced.

3.4 Compression set properties

According to expectations, adding mHNTs stiff filler to NR/EPDM elastomer nanocomposites likewise boosts their hardness and compression set, however the resilience of the nanocomposites showed a diminishing trend as HNTs content rose. According to ASTM D 395, compression set is the material’s continued deformation after the compressive force has been removed. Compression set, which is a permanent set of rubber compounds, is defined by Smith [85] and Othman [86] as a measurement of the rubber’s capacity to maintain its elastic properties under a given set of conditions, including continuous compression at a constant strain. According to Fig. 7, which indicates that the chemical structure of the compound filled with 10 phr of mHNTs is more stiff than the others, the compression set of filled nanocomposites increases in value as filler content does.

In fact, the presence of mHNTs limits the deformability of elastomer chains. With an increase in mHNT loading, the compression set rises, which is consistent with the observed decreased resilience. The compound's flowability under load at a high temperature account for the enhanced compression set. The elastomer’s oil content or significantly lower molecular weight makes the composite more plastic. The best material is the one with the lowest percentage of compression set; for any loading, the best performance is provided by NR/EPDM composites filled with 0 phr mHNT at 23 °C. With increasing mHNT loading, it is discovered that the values of the compression set increase steadily. Compression set is a well-known additional feature that might reveal the degree of flexibility. The rise in compression set values supports the hypothesis that the inclusion of mHNTs reduces the elasticity of cured rubber composites.

3.5 Swelling properties

The interaction between the filler and rubber matrix is examined using a swelling test. For mHNTs-filled rubber nanocomposites, the swelling measurement in terms of mole percent uptake has been done. The solvents employed included benzene, mesitylene, toluene, xylene, n-pentane, n-heptane, n-hexane, and n-octane as well as chloroform, dichloromethane, and carbon tetrachloride. The fact that each of the eleven solvents differs from the other influenced the selection of these eleven solvents. While n-pentane, n-heptane, n-hexane, and n-octane are aliphatic and chloroform, dichloromethane, and carbon tetrachloride are chlorinated solvents, aromatic solvents include benzene, mesitylene, toluene, and xylene. Figure 8 illustrates the impact of mHNTs loading on the mole percent uptake of both unfilled and mHNTs-filled NR/EPDM nanocomposites with various content: 0, 2, 4, 6, 8 and 10 phr.

The ability of these solvents to dissolve or swell the cured rubber nanocomposites varies depending on whether they are aromatic, aliphatic, or chlorinated. The findings of the aromatic solvent swelling are depicted in Fig. 8(a), which demonstrates that the vulcanizates had higher affinities for benzene, toluene, and xylene than for mesitylene. The compound only comprises NR/EPDM, which swells most in the aforementioned solvents, with the tendency lessening as the ratio of mHNTs concentration increases and as the number of mHNTs in the nanocomposite grows. After loading the mHNTs, the acquired result indicates a declining trend in mole percent uptake. The compound that contains 8 phr mHNTs filler filled NR/EPDM nanocomposite lowered the lowest mole percent absorption. The findings of the aliphatic solvent swelling are shown in Fig. 8(b), which demonstrates that the vulcanizates had higher affinities for n-pentane, n-hexane, and n-heptane than for n-octane. Comparatively to chloroform, the vulcanizates had higher affinities for dichloromethane and carbon tetrachloride, according to the
swelling data for chlorinated solvents in Fig. 8(c). It indicates that the crosslinked density in NR/EPDM nanocomposites increases as a result of the mHNT ratio, which restricts the ability of solvents to permeate the cured nanocomposites. Additionally, it indicates that 8 phr of HNTs in rubber nanocomposites are resistant to solvent penetration. This is because rubber nanocomposites with HNT fillers interact with the rubber matrix more effectively as a result of greater HNT dispersion in the rubber matrix.

Dichloromethane, a chlorinated solvent, is reported to have a greater uptake than aliphatic solvents (n-octane). Chloroform, benzene, toluene, xylene, mesitylene, carbon tetrachloride, n-pentane, n-hexane, n-heptane, and n-octane were found to have the lowest uptake. Dichloromethane had the highest uptake.

In all of the edoema outcomes, it was lower in n-octane. It might be as a result of n-larger octane's molecular weight when compared to other solvents. One of the most significant structural characteristics of a cross-linked polymer is the average molecular weight between the crosslinks, which is calculated from swelling behaviour and is directly proportional to the cross-link density. The cross-link density, denoted by the symbol \( v \), is the volumetric number of elastically active network chains that make up a perfect network. The cross-link density of the mHNTs-filled NR/EPDM nanocomposite increases from 2 to 8 phr after the cross-link density of the unfilled and mHNTs-filled NR/EPDM nanocomposites was calculated using the data obtained (Fig. 9). The cross-link density similarly rises with an increase in mHNT content. The growing filler content of the rubber matrix could be the cause. Toluene has a harder time penetrating the rubber matrix because of the rubber's reduced molecular mobility. In comparison to those containing 10 phr of mHNTs, NR/EPDM nanocomposites containing 8 phr of mHNTs performed better in terms of their cross-link density. In contrast to other mHNTs-filled rubber nanocomposites, the average molecular weight between cross-links was inversely related to the cross-link density, making \( M_c \) at 8 phr of the NR/EPDM-mHNTs nanocomposite relatively tiny.

### 3.6 Morphology

The morphology of the materials was examined by FESEM in order to visualise the dispersion of the mHNTs in the rubber matrix. Figure 10(a) depicts a picture of mHNTs and demonstrates their tube-like shape and clumped character. The tubes themselves remain aggregated because of the very small particles' large surface area. The significantly smaller modified HNT particles are readily evident in Fig. 10(b). While the 8 phr modified HNTs are evenly distributed throughout the rubber matrix, the 10 phr modified HNTs create a tubular aggregated structure. It's noteworthy to note in Fig. 10(d) that the aggregated structure of modified HNTs in the 10 phr modified HNTs is greater than in Fig. 10. (c). These studies show that the compatibilizer (EPDM-g-MA) and modifier (DMS) facilitate compatibility between the two elastomers (NR/EPDM) and modified HNTs. The DMS modified HNTs have chemical structures that are similar to those of the polymers and increase their compatibility with nanofiller due to the presence of carbon-carbon double bonds, which are also present on the surfaces of nanofiller. This makes the filler surface more compatible with the polymers (NR/EPDM/EPDM-g-MA) and less hydrophilic. The surface modification with DMS results in a reduction in surface polarity and enhances the HNTs' dispersion.

### 4. Conclusions

This study's objective was to assess the suitability of using DMS-modified HNTs as filler in NR/EPDM/EPDM-g-MA nanocomposites. In this study, it is suggested that modified HNTs be used as filler in NR/EPDM/EPDM-g-MA nanocomposites to prevent the harmful environmental impacts of modified HNTs. It has been demonstrated that
the inclusion of modified HNTs significantly improves the curing behaviours, mechanical characteristics, and swelling properties of NR/EPDM compounds. The following conclusions can be taken from this study:

- DMS modified HNTs filled NR/EPDM/EPDM-g-MA nanocomposites tend to lower scorch time and optimal cure time. However, minimum torque, maximum torque, torque difference, and cure rate index exhibit the opposite trend with increasing the DMS modified HNTs content in NR/EPDM/EPDM-g-MA nanocomposites.
- The maximal tensile strength, stress at 100% elongation (M100), and elongation at break are reached at 8 phr after the addition of DMS modified HNTs to NR/EPDM/EPDM-g-MA. Any additional accumulation causes the tensile strength, M100, and elongation at break to gradually decline.
- As modified HNTs loading increases, the tear strength and hardness of NR/EPDM/EPDM-g-MA nanocomposites also rise. The rebound resilience of the NR/EPDM/EPDM-g-MA nanocomposites is decreased by the addition of modified HNTs. Abrasion resistance and hardness both depend on filler loading in a comparable way.
- As the amount of modified HNTs in a rubber compound rises, the compression set does as well. The loading of modified nanotubes also affects the accelerated ageing behaviour of rubber nanocomposites filled and unfilled with modified HNTs when compressed for 24 hours at 70°C and 100°C.
- The mole percent uptake of NR/EPDM/EPDM-g-MA nanocomposites rose up to 8 phr with the addition of HNTs. The higher cross-link density of modified NR/EPDM/EPDM-g-MA nanocomposites packed with HNTs is the cause of the lower mole percent uptake. With an increase in the amount of modified HNTs, the chemical cross-link density increases.

Overall findings indicate that HNTs may be a more effective nanofiller for strengthening rubber composites. However, 8 phr of modified HNTs nanotubes should be employed to produce superior reinforcement.

**Declarations**

**Ethics approval**

Not applicable.

**Consent to participate**

The writers state that participation is not opposed.

**Consent for publication**

The authors say they have no objections about their consent being published.

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Conflict of interest

The authors declare that there is no conflict of interest.

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